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Published in:
Applied Physics Letters

DOI:
10.1063/1.119692

Publication date:
1997

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Citation: Appl. Phys. Lett. **71**, 930 (1997); doi: 10.1063/1.119692
View online: https://doi.org/10.1063/1.119692
View Table of Contents: http://aip.scitation.org/toc/apl/71/7
Published by the American Institute of Physics

Temperature dependent electron-hole recombination in polymer light-emitting diodes

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(Received 17 March 1997; accepted for publication 13 June 1997)

The current density–voltage characteristics of poly(dialkoxy *p*-phenylene vinylene) based polymer are investigated as a function of temperature. Model calculations show that the differences between single and double carrier devices can be well understood by taking into account a bimolecular recombination process. It is found that the bimolecular recombination is thermally activated with an identical activation energy as measured for the charge carrier mobility. This demonstrates that the recombination process is of the Langevin type, and explains why the conversion efficiency (photon/carrier) of a polymer light-emitting diode is temperature independent. © *1997 American Institute of Physics.* [S0003-6951(97)02133-5]

The discovery that conjugated polymers can be used as the active material in light-emitting diodes (LEDs) has opened the route towards easy processable and mechanically flexible large-area applications, based on polymer LEDs (PLEDs).[1,2] Attention has especially been focused on the poly(*p*-phenylene vinylene) (PPV) derivatives as a result of their large conversion efficiency of 1% to 2% photons/charge carrier. For an optimization of the device performance, a thorough understanding of the device properties is required. Recently, we have demonstrated that in our PPV based devices at low electric fields the transport of holes is limited by space charge effects in the polymer layer.[3] At high electric fields, the hole transport is governed by a combination of space-charge effects and a field dependent mobility,[4] which is thermally activated. The electron current on the other hand is found to be limited by the presence of traps.[3] Thus in contrast to conventional semiconductor LEDs, the charge transport in a PLED is strongly dependent on temperature.

Let us first discuss the influence of temperature on the device performance of a PLED without traps and with a field-independent mobility. Due to space-charge effects, the single-carrier hole-only current J is given by[5]

$$J=\frac{9}{8}\,\epsilon\mu_p\,\frac{V^2}{L^3}, \tag{1}$$

with $\epsilon=\epsilon_0\epsilon_r$ the permittivity of the polymer and μ_p the hole mobility. For a double-carrier device, two additional phenomena become of importance, namely recombination and charge neutralization. We will assume that the recombination is bimolecular, i.e., that its rate is proportional to the product of the electron and hole concentrations. Due to charge neutralization, the total charge may far exceed the net charge. As a result, the current density in a double-carrier device can be considerably larger than in a single-carrier device. In the plasma limit, the current is given by[5]

$$J=\left(\frac{9\pi}{8}\right)^{1/2}\epsilon\left(\frac{2q\mu_p\mu_n(\mu_p+\mu_n)}{\epsilon B}\right)^{1/2}\frac{V^2}{L^3}, \tag{2}$$

with μ_n the electron mobility and B the bimolecular recombination constant. Upon increasing B, the amount of neutralization decreases, so that J becomes smaller. The difference in current between a single- and a double-carrier device provides direct information about the strength of the recombination process. Let us assume that the mobility is thermally activated and that $\mu_p=\mu_n$. The temperature dependence of the hole-only current [Eq. (1)] is directly governed by μ_p whereas the LED current [Eq. (2)] is determined by $\mu_p^{3/2}/B^{1/2}$. Thus for a constant B, the relative difference between a single- and a double-carrier device is expected to decrease with decreasing temperature.

In the present study, the temperature dependence of the charge transport in polymer devices is investigated by performing $J-V$ measurements on both hole-only and double-carrier devices. We demonstrate that there is a bimolecular recombination mechanism of the Langevin type, where the rate limiting step is the diffusion of oppositely charged particles towards each other in their mutual coulomb field. The occurrence of Langevin recombination clarifies why the conversion efficiency (photon/charge carrier) of a PLED is temperature independent, in spite of the thermally activated charge transport. Langevin recombination may be expected for organic hopping conductors[6] and has recently been included in an analytical model for PLEDs.[7] However, we do not know of any temperature-dependent experiments which are essential to demonstrate its occurrence in PLEDs.

The devices under investigation consist of a single polymer layer sandwiched between two electrodes on top of a glass substrate. The polymer is soluble poly(dialkoxy-*p*-phenylene vinylene)[8] (PPV) and is spin coated on top of the patterned indium-tin-oxide (ITO) bottom electrode. For the hole-only devices, an evaporated Au contact is used, so both the electrodes have a work function close to the valence band of the conjugated polymer. For the double-carrier devices, an evaporated Ca contact is used, which has a work function close to the conduction band of the PPV. The $J-V$ measurements are performed in a nitrogen atmosphere in the temperature range of 200–300 K using a HP 4145A semiconductor parameter analyzer. In Fig. 1, the $J-V$ characteristics of both an ITO/PPV/Au device and an ITO/PPV/Ca device are shown for various temperatures. The thickness of

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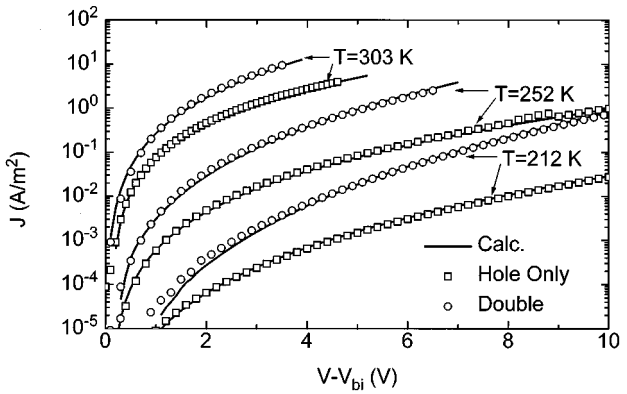

FIG. 1. Experimental and calculated (solid lines) $J-V$ characteristics for an ITO/PPV/Au hole-only device (squares) and an ITO/PPV/Ca double-carrier device (circles) with a thickness of $L=280$ nm at $T=303$, $T=252$, and $T=212$ K. The double-carrier $J-V$ characteristics are corrected for a built-in voltage V_{bi} of 1.5 eV which arises from the work function difference between the ITO and the Ca contact. The hole-only device is modeled using SCLC in combination with a field dependent mobility according to Eqs. (6) and (7), the double injection current is numerically solved from Eqs. (3) to (8).

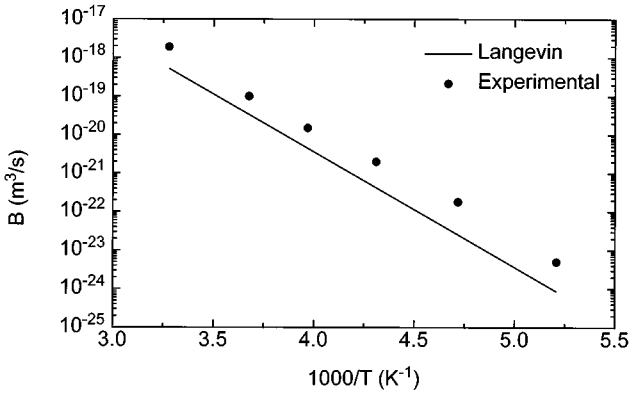

FIG. 2. Temperature dependence of the bimolecular recombination constant (circles) as directly obtained from the $J-V$ characteristics as shown in Fig. 1 using the device model defined by Eqs. (3)–(8). Also shown is the temperature dependence of the Langevin bimolecular recombination constant (solid line) as predicted by Eq. (9) with $\mu_n=\mu_p$.

the polymer layer L amounts to 280 nm. It is obtained that the relative difference between the single- and double-carrier current is rather independent of the temperature, even though according to Eqs. (1) and (2) it is expected to decrease with decreasing temperature.

However, Eq. (2) is not directly applicable to the experimental results of Fig. 1, since electron traps[3] and a field-dependent mobility[4] are not included. Therefore, we present a device model which is characterized by

$$J=q\mu_p[E(x)]p(x)E(x)+q\mu_n[E(x)]n(x)E(x), \tag{3}$$

$$\frac{\epsilon}{q}\frac{dE(x)}{dx}=p(x)-n(x)-n_t(x), \tag{4}$$

$$\frac{1}{q}\frac{dJ_n}{dx}=-\frac{1}{q}\frac{dJ_p}{dx}=Bp(x)n(x). \tag{5}$$

In the above equations, $p(x)$ and $n(x)$ represent the density of mobile holes and electrons, $n_t(x)$ the density of trapped electrons, and $E(x)$ the electric field as a function of position x. According to Eq. (5), we assume that only the mobile electrons recombine. For ohmic contacts, we have the boundary condition[3] $n(L)=N_c$ and $p(0)=N_v$, with the effective density of states in the conductance (N_c) and valence (N_v) band estimated to be 2.5×10^{19} cm^{-3}. The set of Eqs. (3)–(5) can be solved numerically.

In Ref. 4, it was found that the mobility of holes in PPV is given by

$$\mu_p(E)=\mu_0\exp\left(-\frac{\Delta}{kT}\right)\exp(\gamma\sqrt{E}), \tag{6}$$

$$\gamma=\beta\left(\frac{1}{k_BT}-\frac{1}{k_BT_0}\right). \tag{7}$$

The $J-V$ hole-only data as shown in Fig. 1 imply that the activation energy $\Delta=0.59$ eV, the prefactor $\mu_0=0.17$ m^2/V s, the coefficient $\beta=3.1\times10^{-5}$ eV(m/V)$^{1/2}$ and that $T_0=540$ K. The theoretical curves agree well with the experimental data. In Ref. 3, we have shown that the electron conduction is severely limited by the presence of traps. The traps are exponentially distributed in energy with a characteristic energy kT_t and density N_t, so that[5]

$$n_t(x)=N_t\left[\frac{n(x)}{N_c}\right]^{T/T_t}. \tag{8}$$

For our material,[3] $T_t=1500$ K and $N_{t0}=5\times10^{17}$ cm^3. Furthermore, we will assume that $\mu_n=\mu_p$. As a result, the calculated double-carrier current is only dependent on the bimolecular recombination constant B. In an earlier study[9] performed at room temperature on a thinner PLED ($L=130$ nm), it was found that $B=2\times10^{-12}$ cm^3/s.

The experimental results in Fig. 1 for the double-carrier device can be modelled from Eqs. (3)–(8), with B as the only unknown parameter. Clearly, our theory is in good agreement with experiment over a large voltage and temperature range. The obtained values for the bimolecular recombination constant B are shown in an Arrhenius plot in Fig. 2. For our present PPV device ($L=280$ nm), again a $B=2\times10^{-12}$ cm^3/s has been obtained at room temperature. We observe that B is thermally activated with an activation energy equal to that of the charge carrier mobility $\Delta=0.59$ eV. This result strongly indicates that the recombination strength in a PLED is of the Langevin type,[10] i.e., diffusion controlled. Such a behavior is characteristic for materials in which the mean free path of the charge carriers is smaller than a critical distance $r_c=q^2/4\pi\epsilon kT$ at which the Coulomb binding energy between an electron and hole equals $-kT$. In our PPV, the mean free path amounts to the distance between the conjugated sites which is of the order of 10 Å, whereas r_c amounts to 185 Å at $T=300$ K ($\epsilon_r=3$). As a result, the rate limiting step in the bimolecular recombination process is the diffusion of electrons and holes toward each other in their mutual coulomb field. This implies for the recombination[10]

$$B=\frac{q}{\epsilon}(\mu_n+\mu_p), \tag{9}$$

which is also plotted in Fig. 2. The B as determined from our $J-V$ characteristics are slightly (factor 3 to 4) larger than the

values predicted by Eq. (9). A possible explanation for this small discrepancy might be the fact that recombination from trapped electrons may play a role as well. In organic LEDs based on metal chelate complexes (Alq), it has recently been proposed that the recombination originates from trapped electrons.[11] Inclusion of trapped electrons in our model through Eq. (5) gives rise to an enhancement of the recombination strength which leads to a decrease of B in order to describe the double-carrier $J-V$ characteristics of Fig. 1. However, our model calculations show that a full participation of the trapped electrons leads to large deviations from the experimental results. Nevertheless, a small contribution of the trapped electrons to the recombination cannot be excluded and will be the subject of further research.

It should be noted that by including Langevin recombination [Eq. (9)] into Eq. (2) the double-carrier current $J \sim (\mu_n \mu_p)^{1/2}$, which for $\mu_p = \mu_n$ means that J is proportional to μ_p instead of $\mu_p^{3/2}$. An equal temperature dependence for the hole-only and the double-carrier device is the result, in agreement with the experimental results shown in Fig. 1. In fact, the temperature independence of the difference between the single- and double-carrier current is a direct demonstration that the recombination process is proportional to the charge-carrier mobility.

According to Eq. (6), the charge carrier mobility in a PLED is enhanced by the applied electric field. Interestingly, we find that the Langevin recombination constant B is independent on electric field. Clearly, an applied electric field only enhances the diffusion of electrons and holes towards each other in one direction. The diffusion in the directions perpendicular to the field is not enhanced which is the rate-limiting step for recombination at high fields.

Finally, we discuss the consequences of Langevin recombination for the device performance of a PLED. In Fig. 3, the measured conversion efficiency (CE), defined as photon/charge carrier, is shown for a PLED with $L = 110$ nm at various temperatures. It appears that the CE of a PLED is independent of the temperature, in contrast to conventional semiconductor LEDs. This typical behavior of a PLED is a direct consequence of the occurrence of Langevin recombination. In a space-charge limited device as our PLED, the number of charge carriers is mainly determined by the applied voltage and not by the temperature. As a result, the device current is only dependent on temperature by means of the charge carrier mobility. Since the recombination mechanism is of the Langevin type, both the recombination strength and the device current are thermally activated by means of the charge carrier mobility. Since in PPV the photoluminescence efficiency is not dependent[12] on temperature in the range of 200–300 K, the resulting CE of a PLED is temperature independent. The CE increase at low voltages, where electrons are trapped close to the electron injecting contact, is suggested to originate from additional nonradiative recombination losses at the cathode interface.[9]

Furthermore, our model calculations reveal that the recombination efficiency in a PLED resulting from Langevin recombination approaches unity, making PLEDs efficient devices in agreement with earlier estimates by Albrecht and Bässler.[13] By comparing the total number of recombinations inside the PLED with the actual light output, we find that only about 5% of the total recombinations actually contributes to the light output of the device. This large contribution of nonradiative processes is mainly responsible for the relatively low external CE of 2%–2.5%, which also includes out coupling losses.

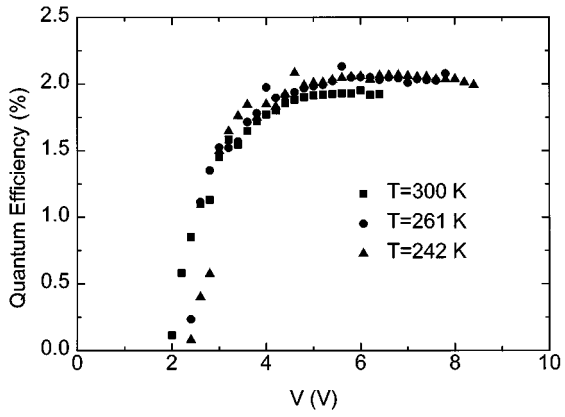

FIG. 3. External quantum efficiency (photons/carrier) vs voltage measured from an ITO/PPV/Ca double-carrier device with a thickness of $L = 110$ nm at $T = 300$, $T = 261$, and $T = 242$ K. The maximum quantum efficiency amounts to 2% and is independent of temperature.

In conclusion, from the temperature dependence of the $J-V$ characteristics, we have demonstrated that the recombination mechanism in a PLED is of the Langevin type. Due to this diffusion controlled recombination, PLEDs exhibit, in contrast to conventional inorganic LEDs, a temperature independent recombination efficiency. Enhancement of the PLED performance can be obtained by decreasing the nonradiative recombination processes, which limit the maximum external conversion efficiency.

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